

Advanced Low-Temperature Sorbents for Fluid-Bed Applications

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Abstract

The Integrated Gasification Combined Cycle (IGCC) process is emerging as the most promising technology for advanced electric power generation from coal that is likely to replace conventional coal combustion. The commercialization of this technology and realization of its full potential, however, depend to a great extent on the development of regenerable sorbents capable of reducing the H₂S content of gasifier fuel gas from several thousand ppmv levels down to a few ppmv at elevated temperatures (i.e., >350°C), over hundreds or even thousands of sulfidation/regeneration cycles.

Over the last two decades, development of high temperature regenerable desulfurization sorbents has been pursued, primarily using various combinations of transition metal oxides. The primary focus has been directed toward applications above 550°C, limiting the choice of metal oxides to those which possess favorable thermodynamic equilibria. These efforts led to the emergence of zinc-based sorbents, such as zinc titanates, as the leading candidates. However, because of problems with sorbent deterioration, further improvement is needed to minimize the overall cost of desulfurization in the IGCC process.

Recent studies on total IGCC system integration have indicated that system components become prohibitively expensive with increasing operating temperature and that the overall process efficiency gains of conducting desulfurization at above 550°C may not be sufficient to justify operation at such high temperatures. The optimum desulfurization temperature appears to be in the range of 350° to 550°C, where technical viability and process efficiency result in lower overall process costs. In addition, because of the more favorable thermodynamic equilibria at the lower temperature range, a large number of metal oxides can be considered for coal gas desulfurization, increasing the likelihood of developing suitable sorbents.

The three most advanced reactor configurations for hot gas desulfurization include fixed-bed, moving-bed, and fluidized-bed systems. The fluidized-bed approach offers advantages over the moving-bed and fixed-bed reactors because of its ability to control temperature, particularly during the highly exothermic regeneration step; however, a more durable, attrition-resistant sorbent is required.

This paper discusses the results obtained in an ongoing study geared towards developing advanced mixed-metal oxide sorbents for desulfurization of coal-derived fuel gases in the temperature range of 350° to 550°C. The paper focuses on the study related to the development of highly attrition-resistant sorbents suitable for fluidized-bed application and addresses the physical and chemical characteristics of a number of novel sorbents as well as their sulfidation performance and regenerability based on extensive thermogravimetric analysis and testing in packed-bed reactors.

Introduction

Coal is used predominantly for power generation with coal-fired power plants currently accounting for approximately 56% of the electricity used in the United States.^[1] In addition, with diminishing petroleum supplies, public concern regarding the overall safety of nuclear power, and unavailability of alternative large-scale sources of energy, coal is gaining much more importance in the total energy picture.^[2] The most economical use of coal in the future is likely to continue to be the generation of electricity.

Current methods for the conversion of chemical energy in coal to electrical energy tend to be cumbersome, wasteful, and environmentally unsound. Coal-fired power plants are inherently only 30 to 35% efficient. In addition, because of increasingly stringent government regulations for sulfur emissions, stack gas desulfurization has been practiced more commonly to meet air pollution emission standards. Although this practice helps the utilities comply with environmental requirements, it lowers plant operating efficiency and reliability, in addition to increasing both capital and operating costs. Furthermore, solid waste streams are generated and must be disposed of in increasingly expensive landfill space.

The limitations of coal-fired power plants have been the main driving force behind technological innovations aiming at improving both the efficiency and environmental performance of power generation from coal. Emerging technologies, such as the Integrated Gasification Combined Cycle (IGCC), are based on coal gasification rather than combustion and require that the sulfur-bearing species (mainly H_2S) be removed at high temperatures to conserve the sensible heat in the gasifier fuel gas, thereby making the process more efficient. In addition, it is economically and environmentally desirable to use regenerable sorbents for H_2S removal.

The major coal reserves that are most readily accessible to industry and population centers are the mid-western coals of Illinois, Western Kentucky, Indiana, and Iowa. Unfortunately, these coals have sulfur levels that are too high for direct utilization. Emerging technologies for power generation essentially eliminate the need for coal preparation to reduce its sulfur content and are therefore creating a renewed interest in these high-sulfur coals.

One of the main obstacles in the commercialization of high-temperature desulfurization systems for IGCC power generation processes remains to be the development of regenerable sulfur sorbents with suitable physical and chemical characteristics. The focus of much of the current research on hot coal-derived fuel gas desulfurization processes has been on the use of zinc-based sorbents. Although these sorbents have been the subject of extensive pilot-scale and process development work, zinc-based sorbents have been shown to suffer from sulfate formation and zinc volatilization, leading to sorbent degradation over multicycle use, increasing sorbent replacement costs and the overall cost of hot gas desulfurization processes. Therefore, investigation of non-zinc based sorbents is now recognized as a logical approach to develop an effective alternative to zinc-based sorbents.

The three most advanced reactor configurations for hot gas desulfurization include fixed-bed, moving-bed, and fluidized-bed systems. The fixed-bed approach has been shown to reduce the

H₂S content of the cleaned gas to very low levels; however, its operation is not continuous, suffers from operational problems, and requires large-scale high temperature valves. To overcome these problems, moving-bed as well as fluidized-bed hot gas desulfurization research has been pursued in recent years. The fluidized-bed approach offers advantages over the moving-bed and the fixed-bed reactors because of its ability to control the reactor temperature particularly during the highly exothermic regeneration step. Commercial hot coal gas desulfurization processes are likely to rely on fluidized-bed technology.

The key characteristic of concern in the fluidized-bed application is the maintenance of sorbent physical integrity during the chemical transformations associated with sulfidation/regeneration. Consequently, both the crush strength of a candidate sorbent and its effective sorption capacity after repeated cycling are of critical interest. Unfortunately, most methods of sorbent formulation examined yielded products that were either too weak or had inadequate capacity. Typically, the reactivity of sorbents with good attrition resistance and adequate capacity was marginal at 550°C and, although reactivity increased with temperature, an excessive weakening occurred as well. Extensive research appeared to verify that excessive attrition results primarily from structural changes during chemical transformations and not from mechanical forces.^[3,4] The excessive temperature and severe chemical conditions of air-steam regeneration tend to be deleterious to many inorganic support materials and sorbent compounds.

The overall efficiency of the IGCC process increases with increasing temperature; however, because of process equipment limitations and other process variables such as fuel gas alkali content, the optimum desulfurization temperature appears to be in the range of 350° to 550°C. Recently, a number of investigators argued that the benefit to be gained by lower temperature application may outweigh the slight loss of efficiency, resulting in lower overall cost of electricity; desulfurization temperatures in the range 350to 550°C have been recommended.^[5,6]

At these lower temperatures, although the extent of desulfurization improves through more favorable thermodynamic equilibrium, the reactivity of the sorbent is diminished because the kinetic mechanisms for sulfidation experience an Arrhenius-type decrease with decreasing temperature. Therefore, a highly reactive sorbent is needed for these lower temperature applications.

Objectives

The overall objective of this program is to develop regenerable sorbents for use in the temperature range of 350° to 550°C to remove hydrogen sulfide (H₂S) from coal-derived fuel gases using fluidized-bed reactors.

The sorbents must have the chemical characteristics necessary to permit cyclic use without a drastic loss of reactivity and also the physical characteristics that are compatible with a fluidized-bed environment. These chemical and physical characteristics should also remain acceptable during absorption and regeneration. The sorbents must be capable of removing H₂S to less than 20 ppmv over the temperature range of 350° to 550°C and pressures in the range of 1 to 20 atm, and at least function satisfactorily at the lower end of the temperature range.

Under Contract Option, at least one fluidized bed formulation will be tested for long-term (at least 100 cycles) durability and chemical reactivity in a fluidized-bed bench-scale unit. A state-of-the-art high-pressure/high-temperature reactor (HPTR) with 5 to 7.5 cm inside diameter is currently available at IGT. This unit is capable of operation in bubbling fluidized bed, as well as fixed-bed mode.

Approach

The chemical composition of formulations is based on available literature data and previous studies at IGT. The selection of the “major active compounds” (oxides) is based on the thermodynamic equilibrium and chemical reactivity in the temperature range of 350° to 550°C, while the selection of the “minor compounds” is based on rendering of superior physical and chemical properties such as attrition resistance, pore structure, etc. The general approach consists essentially of selecting cost effective sorbents that can remove H₂S to below 20 ppm in fluidized-bed application in the specific temperature range and at pressures up to 20 atm. Small quantities of each formulation are prepared for physical and chemical characterization and initial screening tests in a 1-inch fixed-bed/fluidized-bed reactor, as well as the state-of-the-art high-pressure/high-temperature thermogravimetric analyzer (HPTGA) available at IGT. This latter unit is capable of operation at temperatures up to 1000°C and pressures up to 100 atm using very small quantities of solids and very high flow rates of gas, thus eliminating the “starvation condition” and “gas film diffusion” that are very common in high pressure TGA experiments.

Sorbents used in a fluidized bed application must be in the form of attrition resistant granules which retain the fine powder chemical reactivity. A number of commercial granulation techniques are available, but the technique to be applied for sorbent preparation are limited to those which produce small, 50-300 micron, granules with high attrition resistance. Small batches of the sorbent are prepared in this study in equipment with direct commercial-scale counterparts.

Granulation techniques include the general categories of rotating pans and drums, fluidized-bed formation, extrusion, compaction, and high-shear mixing. In each of these methodologies, control of moisture content, particle size, the addition of binders, and post-production heating or calcining can be used to create granules with desired properties. The selection of the appropriate granulation technique is based on the composition of the formulation chosen in this study.

The attrition resistance of a sorbent material is one of the key factors in determination of the life of the sorbents. Therefore, attrition tests are made to determine before reactor testing which materials are comparatively hard enough for experimentation. Attrition resistance can be measured by a modified high-velocity jet method used by others,^[7] as well as proprietary methods developed at IGT.

Project Description

Thermodynamic and practical considerations of direct relevance to the present investigation have previously been addressed in detail.^[8,9] Combination of findings from several studies identified a

large number of metal oxides that are capable of reducing the H₂S level of the fuel gas to below 20 ppmv for IGCC application in the temperature range of 350°-550°C. The main criteria imposed for selection of potential metal oxides were:

- Favorable thermodynamic equilibrium in the temperature range of 350 to 550°C;
- Minimization of undesired reactions under reducing gas conditions, such as interactions with HCl, CO, and H₂, and catalysis of gas phase reactions;
- Feasibility and ease of complete conversion of metal sulfide to oxide (regeneration); and
- Minimization of undesired reactions under regeneration conditions, such as sulfate formation and hydrothermal instability.

While the number of metal oxides with enough potential to warrant further investigation is large, only those metals listed as main components in Table 1 have been given immediate attention in this study, primarily because of economic considerations and the likelihood of developing effective sorbents. These selected metals were then divided into three functional groups, as shown in Table 1, to serve as guidelines for determining the relative compositions of sorbent formulations:

- Main reactive components for desulfurization
- Secondary components (reactive or non-reactive) to provide chemical stability and promote porosity
- Inert structural components to maintain durability as the sorbent is recycled.

Table 1. List of main, secondary, and structural metal components for sorbent screening

Main Component	Secondary Component	Structural Component
Cu, Fe, Mn, Zn	Cu, Fe, Mo, Mn, Ni	TiO ₂ , ZrO ₂ , Al ₂ O ₃ , MgO, etc.

Sorbent Preparation and Screening

A systematic approach was used to prepare and screen the sorbents for fixed-bed testing as well as thermogravimetric analysis. Formulation parameters considered in preparing the sorbents included sorbent composition, preparation technique, and induration conditions.

Sorbent compositions were first selected from the three functional groups shown in Table 1. Commercially available sorbents of similar relative compositions were also included. The supports shown here are selected based on their capability to provide adequate structural strength and sintering resistance to reduce attrition and retain the reactivity of the sorbent. These sorbent formulations were geared toward enhancement of the attrition resistance and/or lowering of the regeneration temperature, while maintaining acceptable reactivity toward H₂S in the temperature range of 350° to 550°C.

After preparing the sorbents their mechanical strengths were compared with that of United Catalyst zinc titanate sorbent (UCI-4169), considered here to be the baseline sorbent for mechanical strength. This sorbent has been shown in previous studies to have adequate attrition

resistance for fluidized-bed application.^[10,11] If the mechanical strengths of the prepared sorbents were not at least comparable to that of the UCI zinc titanate, the sorbent formulation was modified and the above step was repeated.

During this study, considerable success has been achieved in extending the application of a pelletization technique previously developed for formulation of spherical pellets (dia.=3-5 mm)^[12] to the preparation of highly attrition resistant granular (dia. = 100 to 850 μ m) sorbents. This sorbent manufacturing technique has been applied to the preparation of copper-, iron-, manganese-, and zinc-based sorbents suitable for fluidized-bed applications at lower temperatures, i.e., $T \leq 550^\circ\text{C}$. During this past year 76 sorbent formulations representing various compositions and preparation techniques have been prepared. The breakdown of these formulations in terms of the main reactive metal oxide is shown in Table 2. A number of the indicated formulations had mechanical strength equal to or better than that of the UCI zinc titanate sorbent. These were evaluated for H_2S removal efficiency and effective sulfur capacity.

Table 2. Breakdown of Formulations Prepared (this Year)

Main Reactive Metal Oxide	No. of Formulations Prepared
Fe_2O_3	5
CuO	6
Mn_2O_3	6
ZnO	59

An Instron Universal Testing Instrument (Model 1011) was used to perform mechanical tests on some of the sorbents that were prepared in the form of spherical pellets. In a typical test, a pellet is loaded onto a loading frame and a moving crosshead applies a load to the pellet at a commanded speed, in accordance with ASTM procedures. A calibrated transducer in the moving crosshead then measures the applied load at breakage. This load is known as the crush strength and is given in force divided by contact length (i.e., N/mm of pellet diameter). The average from 10 to 15 pellets is taken in this study as a representative value of the sorbent crush strength. In the case of sorbents IGTSS-179 and IGTSS-057, for example, these values were 43.5 and 22.5 N/mm, respectively. Table 3 lists crush strength values reported by other investigators and serves as a basis for comparison.

Table 3. Crush Strength Comparisons

Reference No./Sorbent	Crush Strength Reported, N/mm
13	17
14	12 - 32
15	36
16	73
17	23.8
IGTSS-179 (this study)	43.5

Preliminary testing included determination of the sulfidation reactivity and effective sulfur capacity of prepared sorbents to identify potential candidates for high pressure fluidized-bed fuel gas desulfurization. The overall effective capacity is equal to the theoretical sorbent capacity times fractional conversion at breakthrough.

Sorbent sulfidation/regeneration testing was carried out in a quartz packed-bed reactor system at temperatures of 350° to 550°C using a simulated coal-derived fuel gas mixture (Table 4), mostly at a space velocity of 2000 hr⁻¹. The H₂S content of the sulfidation feed gas was increased to 2% to induce early breakthrough. The particle size of the sorbents tested was in the range of 500 to 850 µm during fixed-bed testing, and 250 to 300 µm during thermogravimetric analysis. Sulfided sorbents were regenerated using nitrogen-air mixtures at temperatures of 550°-700°C. The extent of each of the desulfurization and regeneration reactions during fixed bed testing was determined by analyzing the reactor exit gas for H₂S and SO₂, respectively, with a dedicated gas chromatograph equipped with appropriate detectors.

Table 4. Composition of Simulated Coal Gas

Gaseous Component	Vol. %
CO	20
CO ₂	10
H ₂	10
H ₂ O	10
H ₂ S	0.5-2
N ₂	48-49.5

Results

A number of sorbents have been prepared in this project that possess sufficient reactivity, sulfur capacity, and physical durability for IGCC applications at temperatures ≥ 350°C. The physical characteristics of some of these developed sorbents are presented in Table 5.

During this study, it was determined that, because of the high attrition resistance of the sorbents prepared, some of these sorbents required an “activation step” to render their performance at lower temperatures (i.e., 450°C) comparable to, or even better than, that at a higher temperature (i.e., 650°C). A series of tests were conducted in the thermogravimetric reactor (TGA) to determine the optimum activation method. This finding is illustrated in Figures 1 and 2 for zinc-based and iron-based sorbents, respectively, after applying different activation methods. The results indicate that both sorbent reactivity and sulfur capacity increase substantially upon activation by Method C. These results appear to suggest that the sorbent activation technique developed may be a major parameter in the development of attrition resistant sorbents for lower temperature (i.e., T ≤ 550°C) applications. This point is made more evident by the results reported in Figure 3, where the performance of the IGTSS-122 sorbent at 450°C, after the sorbent had been activated, is clearly superior to the performance of the fresh (i.e., no activation) sorbent at 650°C.

It must be pointed out, however, that the “activation” techniques were determined largely from work conducted using thermogravimetric analysis.

As reported in Table 2, sorbent development work in this on-going study focused on zinc-based sorbents to a large extent. A number of effective zinc-based sorbents have been developed for the temperature range of 450° to 550°C. The results from sulfidation performance evaluation in the HPTGA reactor unit at 450°C, following activation, are presented in Figure 4. This preliminary sorbent evaluation was used to identify promising sorbents for further testing in the fixed-bed reactor. Generally, those sorbents achieving a weight gain higher than 3% were further tested.

Table 5. Physical Characteristics of Sorbents Developed at IGT.

Sorbent Designation	Condition	Hg Density, ρ_b (g/cm ³)	Bulk ρ_b	Apparent (Skeletal) Density, ρ_a (g/cm ³)	Porosity (%) [*]	Total Pore Surface Area (m ² /g)	Average Pore Diameter (μ m)
IGTSS-057	Fresh	1.6170		4.6936	65.55	9.2085	1.47
IGTSS-122	Fresh	2.3783		4.5425	47.64	3.9135	7.17
IGTSS-135	Fresh	1.4825		2.6864	44.81	0.3457	TBD
IGTSS-139	Fresh	1.7841		4.6872	61.94	1.6040	5.10
IGTSS-145	Fresh	3.4934		4.7313	26.16	4.4873	TBD
IGTSS-179	Fresh	3.0573		4.1724	26.73	5.2273	16.6
IGTSS-189	Fresh	2.5930		4.9111	47.20	2.0690	1.84
IGTSS-135	Regenerated	1.8146		4.3625	58.40	2.9046	1.51
IGTSS-139	Regenerated	2.2490		4.7878	53.03	1.4916	4.59
IGTSS-189	Regenerated	2.7218		4.8080	43.39	2.4275	2.40

Calculated as $(1 - \rho_b/\rho_a)*100$, or equivalently $asp_b*(\text{Total Intrusion Volume})*100$

The results from testing of one such zinc-based sorbents, IGTSS-189, are shown in Figures 5 through 7. These results indicate the H₂S removal efficiency of this sorbent and its capability of achieving effective sulfur capacities greater than 10 g S/100 g sorbent at 550°C, and from 4 to 8 g S/100 g sorbent at 450°C. In addition, this sorbent was regenerated at 550°C, making it suitable for fuel gas desulfurization in transport as well as bubbling fluidized-bed reactors.

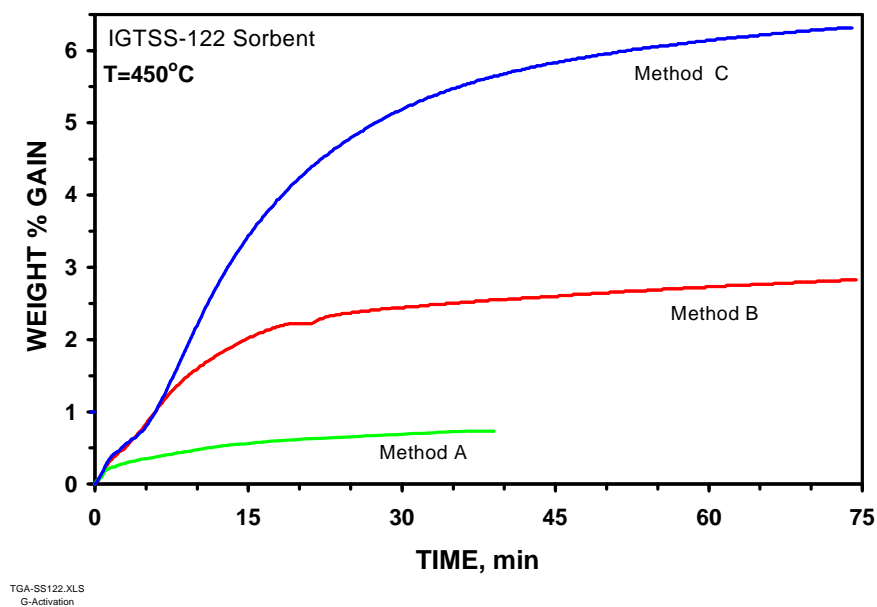


Figure 1. Effect of Fresh Sorbent Activation Method on Subsequent Sulfidation Performance of IGTSS-122 Sorbent at 450°C.

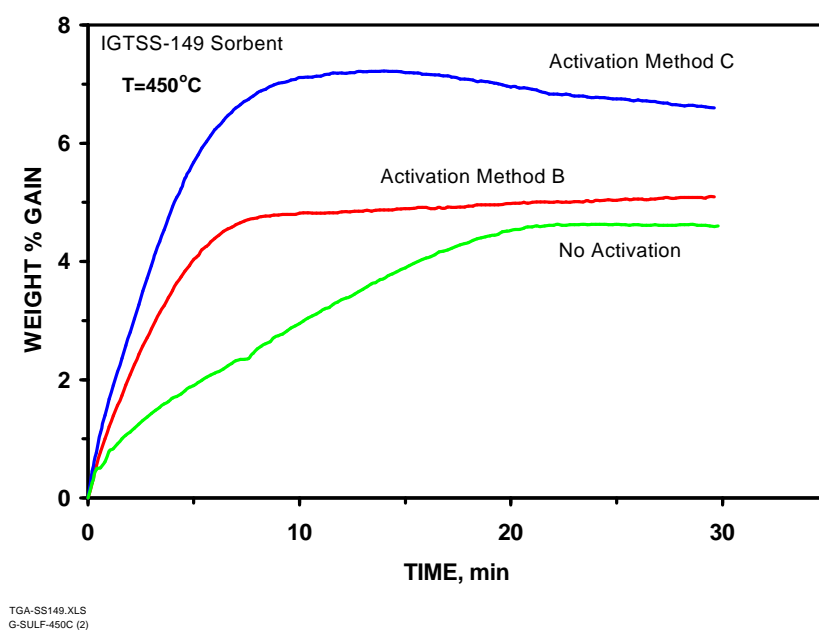


Figure 2. Effect of Fresh Sorbent Activation Method on Subsequent Sulfidation Performance of IGTSS-149 Sorbent at 450°C.

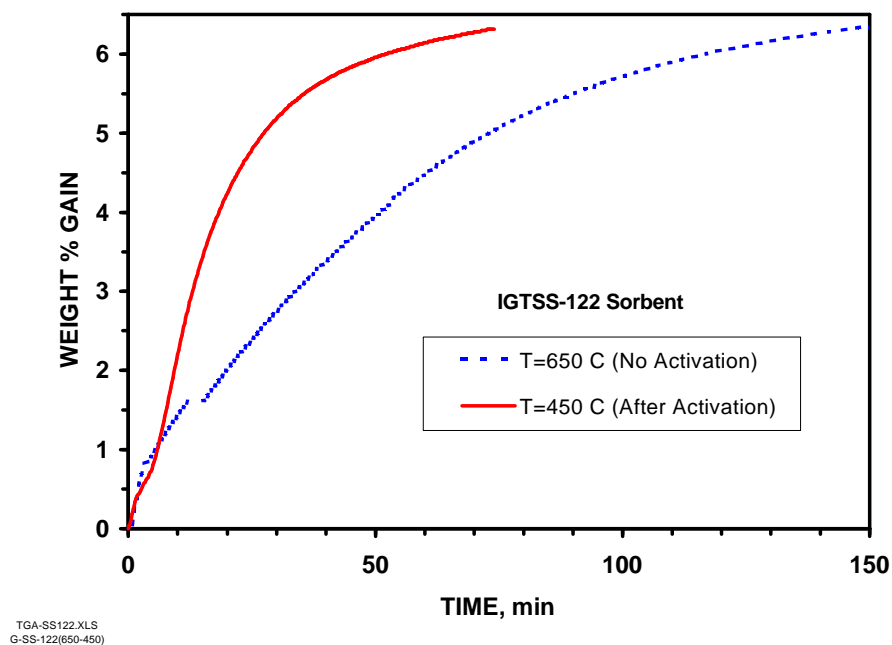


Figure 3. Comparison of Sulfidation Performance of IGTSS-122 Sorbent At 650°C (Before Activation) and at 450°C (After Activation).

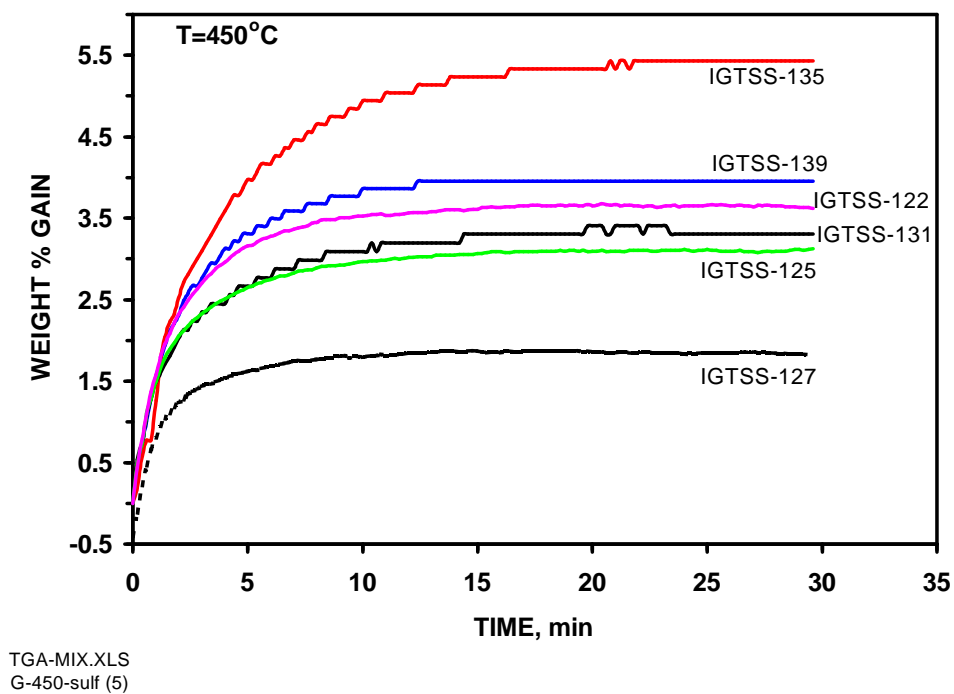


Figure 4. Comparison of Sulfidation Performance via HPTGA Analysis of Several ZnO-Based Sorbents at 450°C

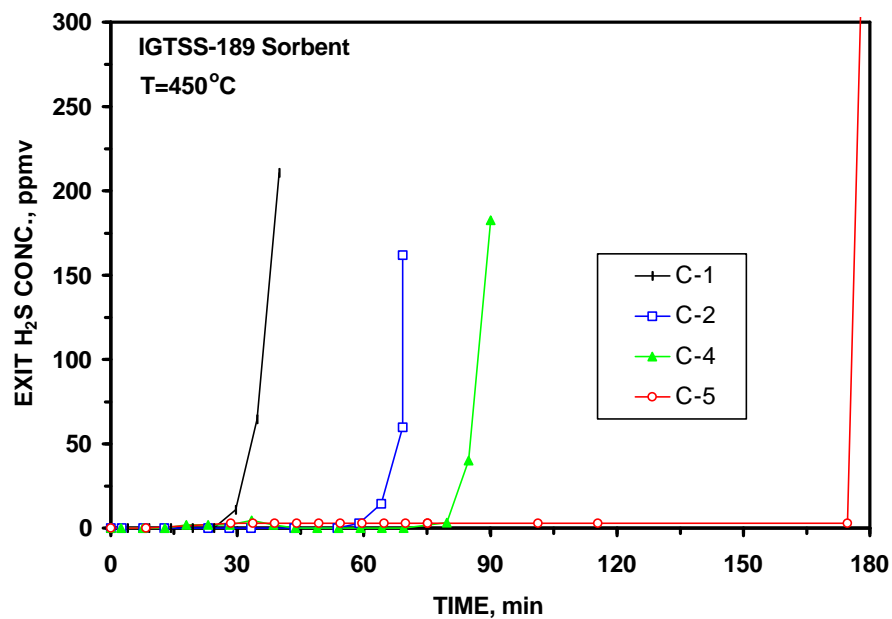


Figure 5. H₂S Breakthrough Curves for IGTSS-189 Zinc-Based Sorbent at 450°C

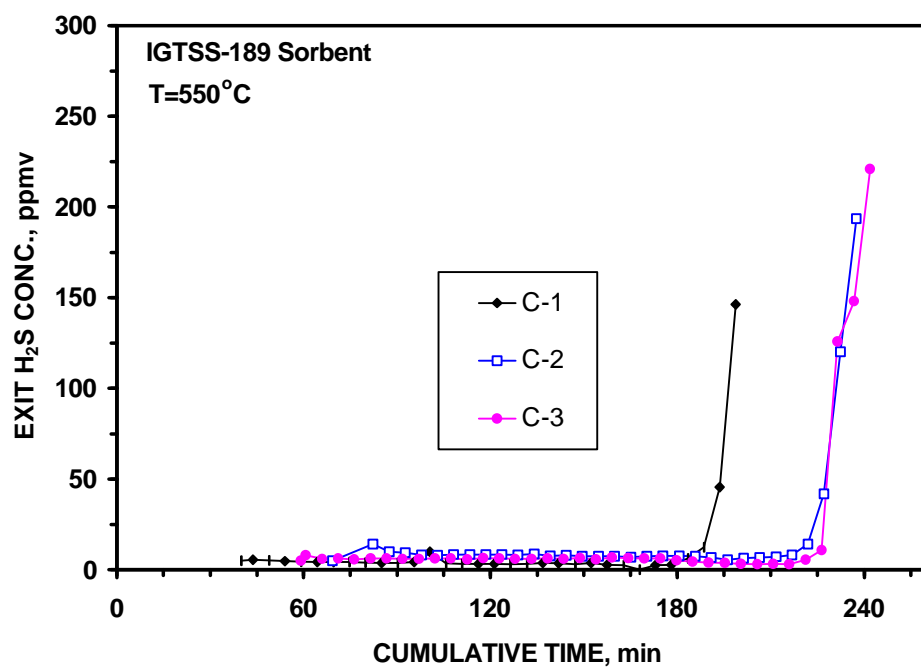


Figure 6. H₂S Breakthrough Curves for IGTSS-189 Zinc-Based Sorbent at 550°C

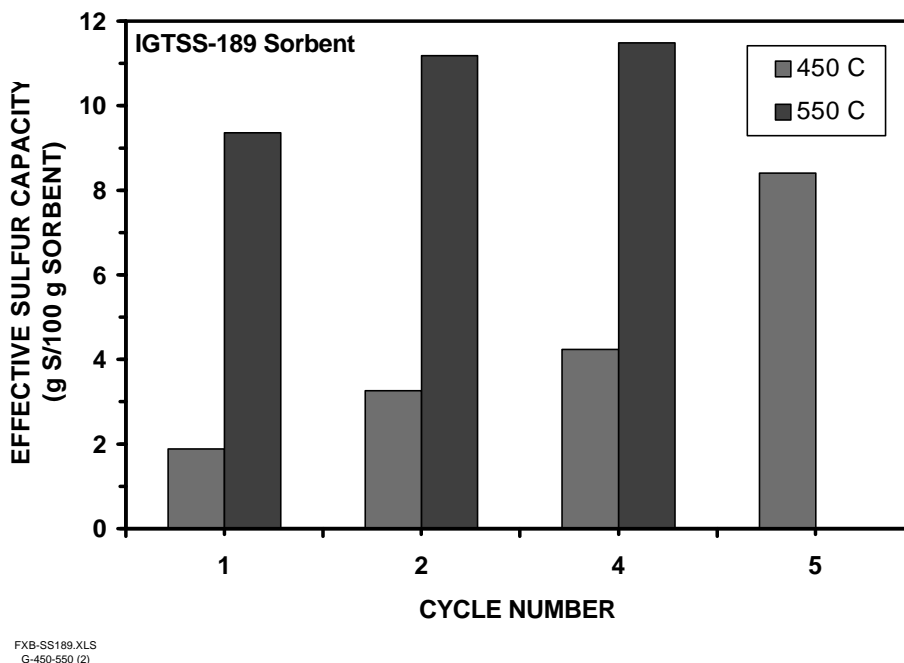


Figure 7. Comparison of Effective Sulfur Capacity of IGTSS-189 Zinc-Based Sorbent at 450 and 550°C

A manganese-based sorbent, IGTSS-057, achieved a total pre-breakthrough time of about six (6) hours in the second sulfidation cycle at 450°C, as shown in Figure 8. This time corresponds to a total sorbent conversion of nearly 47%, at a H₂S breakthrough level of 20 ppmv, and to an effective sulfur capacity of approximately 20 g S/100 g sorbent. This increase in capacity over that seen in the first cycle is likely due to structural changes during sulfidation-regeneration, leading to improved sorbent performance. Also, as shown in Figure 8, IGTSS-057 sorbent, in its fresh condition, performed comparably well at 350°C. To reduce the cycle time during testing of IGTSS-057 sorbent the sulfidation gas space velocity was increased to 6000 hr⁻¹, the space velocity of the O₂-N₂ gas mixture used for regeneration was maintained at 2000 hr⁻¹. The regeneration gas space velocity was not increased to prevent overheating of the sorbent during the highly exothermic regeneration reaction, which would lead to sintering and subsequent loss of reactivity. The results from several cycles are reported in Figure 9. As indicated in this figure, IGTSS-057 performed consistently well even at this higher sulfidation gas space velocity, achieving effective sulfur capacities ranging from 10 to 12 g S/100 g sorbent.

In an on-going research program for development of novel copper-based sorbents at IGT, sponsored mainly by the Illinois Clean Coal Institute (ICCI), Copper based sorbents were produced in granular form, with a much higher attrition resistance compared to a commercial granular zinc titanate sorbent, as well as excellent desulfurization efficiency (i.e., < 5 ppmv H₂S in desulfurized gas).

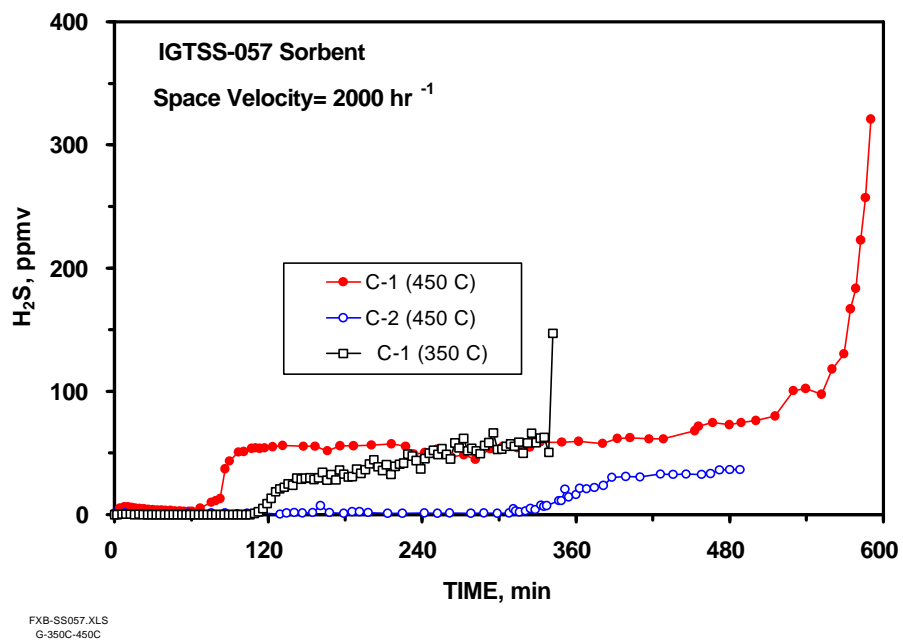


Figure 8. Comparison of Sulfidation Performance of IGTSS-057 Sorbent at 450°C and 350°C

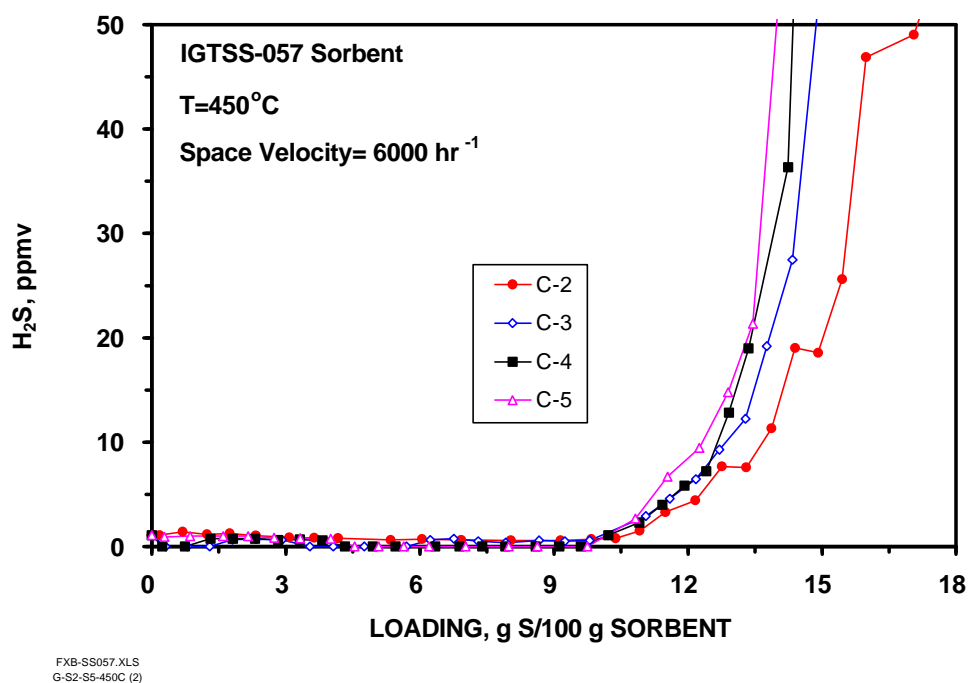


Figure 9. H₂S Breakthrough Curves for IGTSS-057 Manganese-Based Sorbent at 450°C

IGTSS-179, one of a number of copper-based sorbents recently developed at IGT, appears to hold significant promise for fuel gas desulfurization in the temperatures range of 350°-550°C. As shown in Figure 10, limited multi-cycle testing in the fixed-bed reactor at 450°C indicated this sorbent has excellent H₂S removal efficiency and an effective sulfur capacity approximating 7 grams of sulfur per 100 grams of sorbent. The sulfidation performance of IGTSS-179 sorbent at 350°C is essentially comparable to that at 450°C. Figure 11 compares the results obtained from testing two batches of IGTSS-179 sorbent that were made separately, clearly indicating the reproducibility of the sorbent manufacturing technique developed at IGT. It must be pointed out that IGTSS-179 copper-based sorbent did not require an activation step to enhance its reactivity at the lower temperature, despite its significantly high crush strength.

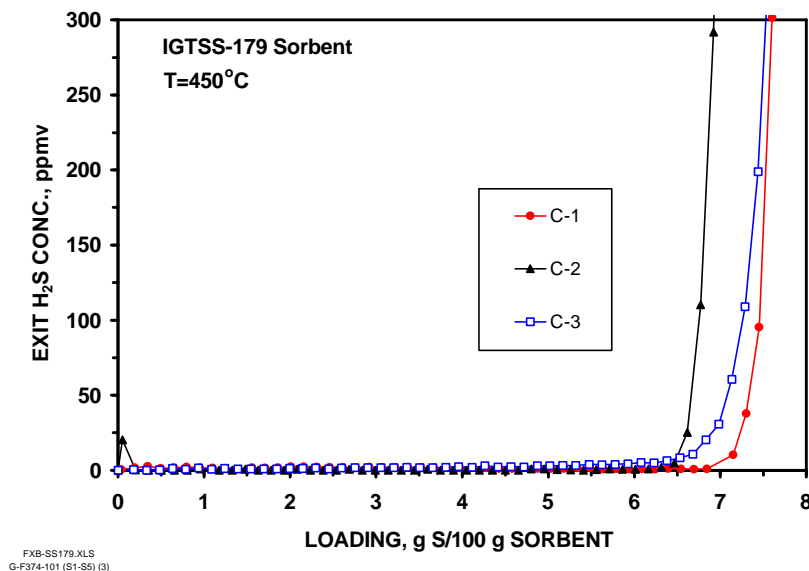


Figure 10. H₂S Breakthrough Curves for IGTSS-179 Copper-Based Sorbent at 450°C

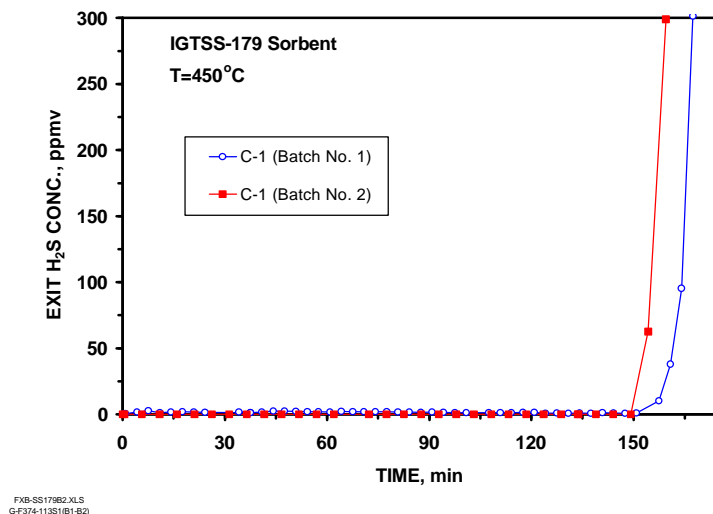


Figure 11. Reproducibility of IGT's Sorbent Manufacturing Technique

Summary and Conclusions

Considerable success has been achieved in extending the application of a pelletization technique previously developed for formulation of spherical pellets (dia. =3-5 mm) to the preparation of highly attrition resistant granular (dia. = 100 to 850 μm) sorbents. This sorbent manufacturing technique has been applied to the preparation of copper-, iron-, manganese-, and zinc-based sorbents suitable for fluidized-bed fuel gas desulfurization applications at lower temperatures, i.e., $T \leq 550^\circ\text{C}$.

Several sorbent formulations developed in this program appear to have desirable physical and chemical properties for effective desulfurization of coal-derived fuel gases in the temperature range of current practical interest (350° to 550°C). Evaluation of the selected sorbent formulations at process conditions in IGT's High pressure bench scale test HPTR unit is currently underway to select the best sorbent formulation for long-term testing .

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